Aromatic B₃ ring stabilized group 2 Dimer, B₃-Y-Y-B₃ (Y = Be, Mg, Ca)Ritam R. Borah^a, Amlan J. Kalita^a, Farnaz Yashmin^a, Kangkan Sarmah^a, Rinu P. Deka^{a,*}, Dimpul Konwar^{b,*}, Ankur K. Guha^{a,1,*}^a Advanced Computational Chemistry Laboratory, Cotton University, Panbazar, Guwahati, Assam 781001, India^b Department of Materials Science and Engineering, Gachon University, Bokjung-dong, Seongnam-si 1342, Republic of Korea

ARTICLE INFO

Keywords:

Aromaticity
sandwich
DFT

ABSTRACT

Quantum chemical calculations have been performed on B₃ ring stabilized Y-Y interaction (Y = Be, Mg, Ca) to understand the possibility of binuclear sandwich type complex formation. Calculations indicate single reference character of the studied systems. The complexes have been found to be stable towards dissociation into different fragments. Thermodynamic consideration also indicates the favourability of their formation.

1. Introduction

Beryllium-beryllium interaction has been one of the most eccentric features among metal-metal interaction. The bond dissociation energy of the Be₂ dimer is rather weak (0.1 eV) [1]. This is due to the fact that the four valence electrons of Be₂ in the X [1] Σ_g ground state occupy the σ_g bonding and corresponding σ_u antibonding orbital resulting in a Be-Be distance of 2.45 Å [1]. However, ultrashort Be-Be distance with little or no bond has been found frequently [2–9]. Cui and co-workers reported that diberyllium difluoride (Be₂F₂) has a very strong Be-Be interaction with bond dissociation energy (BDE) of 76.9 kcal/mol [9]. However, they also reported the shortest Be-Be distance of 1.9 Å in the discus-shaped species Be₂B₈ and Be₂B₇[−] anion without any Be-Be interaction [9]. Multiple bonding with double π bond without a σ bond has also been proposed [10]. Our group has recently confirmed the presence of true triple bond with two π and one σ bond between two Be centres [11]. Thus, it appears that Be-Be interaction is gaining attention despite being a diatomic molecule with formal bond order of zero. Different structural arrangements featuring Be-Be interaction have been proposed [2–12], however, to the best of our knowledge, only a sandwich type structural feature with strong Y-Y (Y = Be, Mg, Ca) interaction has been studied in Cp-Y-Y-Cp (Cp = C₅H₅) by Xie and co-workers [13]. To investigate this possibility, we envisioned that tri-atomic cyclic B₃ cluster with doublet ground state would be a good choice. The presence of one unpaired electron in each B₃ ring is expected to transmute one electron to each Be centre which then would prefer to form a strong Be-Be bond. It deserves a special mention that Brea and co-workers have

shown the formation of super strong Be-Be interaction with radical ligands [12].

It should be pointed out that the chemistry of clusters has been the corner stone of attraction due to their wide range of application ranging from catalysis to energy storage material [14–21]. Atomic clusters gained immense attention due to their ability to form nanomaterials which can be utilized for clean energy sources and in catalysis [21–23]. Cluster composition, electronic configuration and magic numbers are the core focus area of cluster research. One such small atomic cluster is the group 13 element (B, Al, Ga) triatomic clusters which gained recent attention [24–31]. Triatomic B₃ is the building block of many boron-clusters and experimental [26] and theoretical [30] studies have revealed that the ground state of B₃ is doublet. Theoretical studies have also revealed the presence of σ and π aromaticity in B₃ [30,32,33].

Herein, we have undertaken a theoretical study to investigate the possibility of formation of Y-Y (Y = Be, Mg, Ca) interaction in the sandwich type complex, B₃-Y-Y-B₃. Is there any multireference character? How strong is the Y-Y interaction in these complexes compared to that in free Y₂ dimer and its dication? What is the nature of Y-Y interaction? These are some of the questions that will be addressed in this contribution.

2. Computational details

All the molecules were fully optimized without any symmetry constraint at M06-2X/def2-TZVP level of theory [34]. Harmonic frequency calculations were performed at the same level of theory to

* Corresponding authors.

E-mail addresses: rinuprabhadeka@gmail.com (R.P. Deka), dkonwar@gachon.ac.kr (D. Konwar), ankurkantiguha@gmail.com (A.K. Guha).¹ A. K. G. dedicates this work to his maternal uncle Mr. Santosh Kr. Dutta for his eternal soul.

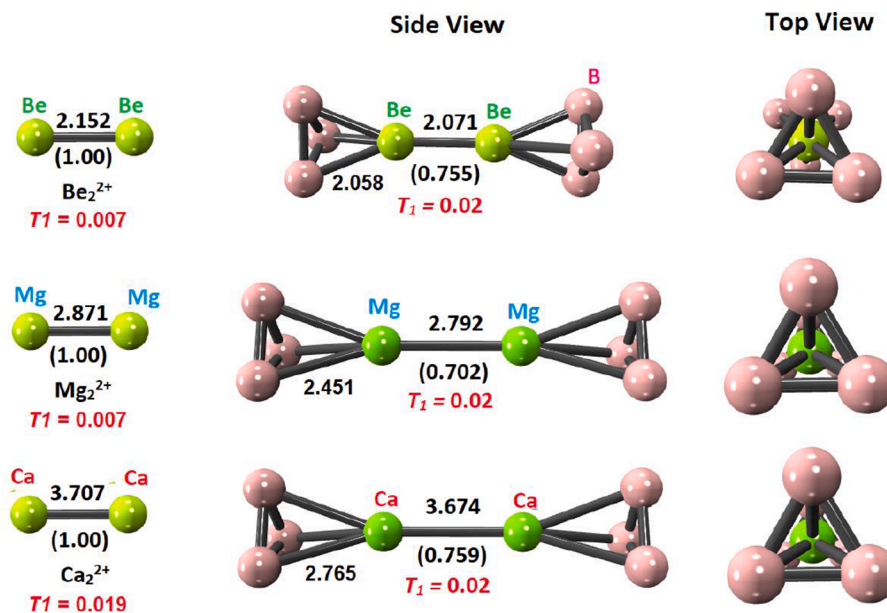


Fig. 1. M06-2X/def2-TZVP optimized geometries of the neutral Y₂ dimer, dication and B₃ ring stabilized sandwich type complexes. Bond lengths are in Å and Wiberg bond index values are given within parenthesis. T₁ diagnostic values at CCSD(T)/def2-TZVP are also given.

understand the nature of the stationary points. All these structures were found to be at their local minima with all real values of the Hessian matrix. Stability of the wave functions was also verified. Natural bond orbital (NBO) calculations were also performed to understand the electronic structure of these systems [35]. Further, energy refinement of the studied systems were performed by running single point calculations at CCSD(T)/def2-TZVP level of theory on the M06-2X/def2-TZVP optimized geometries. Multireference character of these complexes were analyzed on the basis of the T₁ diagnostic values of CCSD(T)/def2-TZVP calculations. All these calculations were performed using GAUSSIAN16 suite of program [36].

Electronic structure of these systems were further analyzed quantum theory of atoms in molecules (QTAIM) [37] and electron localization function (ELF) [38] analyses were also performed. All these are performed using Multiwfn program code [39].

3. Results and discussion

Fig. 1 shows the optimized geometries of the complexes. All these complexes feature η^3 coordination mode. The η^1 coordination modes are higher in energy (Fig. S1, Supporting Information) and η^2 coordination modes are higher order saddle points on the potential energy surface. As Be₂ dimer has been defined as a highly electronically correlated system, we therefore, checked the multireference character of the B₃-Y-Y-B₃ complexes. The T₁ diagnostic values of all these complexes are 0.02 suggesting monoreference characters of the wave functions [40]. The M06-2X/def2-TZVP calculated value of the Be-Be distance (2.152 Å) in Be₂²⁺ is only 0.022 Å longer than that calculated at CCSD(T)/cc-PVTZ level (2.130 Å) [12]. In addition, the T₁ diagnostic values of all the dicationic dimers are <0.02 suggesting single-reference characters of the wavefunction and thereby validates M06-2X/def2-TZVP level to be adequate for this work. There is strengthening of Y-Y interaction from the neutral dimer to their dications as evident from the Y-Y distance. The Y-Y distance becomes even shorter in the B₃-Y-Y-B₃ complexes as compared to their dications. Both top view and side view of the sandwich type complexes are shown in Fig. 1. The Be complex adopts a staggered type structure while Mg and Ca prefer eclipsed type. The eclipsed type structure for Be and the staggered type structures for Mg and Ca are first order saddle point on the potential energy surface. All the Y-Y interactions in the complexes are associated with significant

values of Wiberg bond indexes suggesting strong Y-Y interaction. For all the complexes studied, the Y atom carries positive charge consistent with dicationic character of Y₂. The electronic configuration of Y atom is also consistent with [Ng]ns¹ (Ng = Noble gas). The migration of one electron from σ^*_{YY} orbital to B₃ fragment results in closed-shell character of B₃ as B₃⁻. In B₃-Y-Y-B₃ complexes, each B₃ unit is closed shell implying single reference character, explaining the T₁ diagnostic value of 0.02. It should be noted that the single-reference methods can correctly reproduce the electronic structure of cations. [41] As Y₂ moiety has a dicationic character, it is expected that single-reference method is adequate enough to describe the electronic structure of the studied system.

To investigate the electronic structure of the system, we first carried out natural bond orbital (NBO) analyses [35]. Fig. 2 shows the Kohn-Sham frontier molecular orbitals (MO) along with their eigen values (in eV). All these complexes show similar MOs. The HOMO in every case represents the Y-Y bond. HOMO-1 represents the σ bond delocalized within the B₃ ring. HOMO-2 is the in-phase Be-Be bonding orbital while HOMO-3 is the out-of-phase combination. Thus, HOMO-2 bonding (Be-Be) orbital cancels the HOMO-3 antibonding (Be-Be) orbital. Overall, there is retention of one Be-Be σ bonding orbital. Table 1 summarizes the natural charge at Y and B atoms and electronic configuration of the Y atom. Fig. 2(d) shows the interaction diagram obtained through charge decomposition analysis (CDA) [42]. It reveals the formation of Be-Be σ bonding from the singly occupied molecular orbital (SOMO) of B₃-Be doublet fragments resulting in dramatic lowering in the molecular orbital energy (HOMO) in B₃-Be-Be-B₃ molecule. Rigid potential energy surface scanning with incremental Be...Be distance in both singlet and triplet states reveal that the formation of B₃-Be-Be-B₃ is highly favourable via singlet pathway (Fig. S2, SUPPLEMENTARY INFORMATION). The pairing of singly occupied electrons in B₃-Be fragments resulted in the formation of a strong Be-Be sigma bond in the singlet ground state of B₃-Be-Be-B₃ molecule.

Further the electronic structure of these complexes were analyzed within the framework of quantum theory of atoms in molecules (QTAIM) [37] and electron localization function [38]. QTAIM is based on topological properties of electron density and its derivatives. It describes the bonding process with the help of bond paths and critical points. The electron density (ρ) exhibits a maximum, a minimum, or a saddle point in space. These points are referred to as critical points

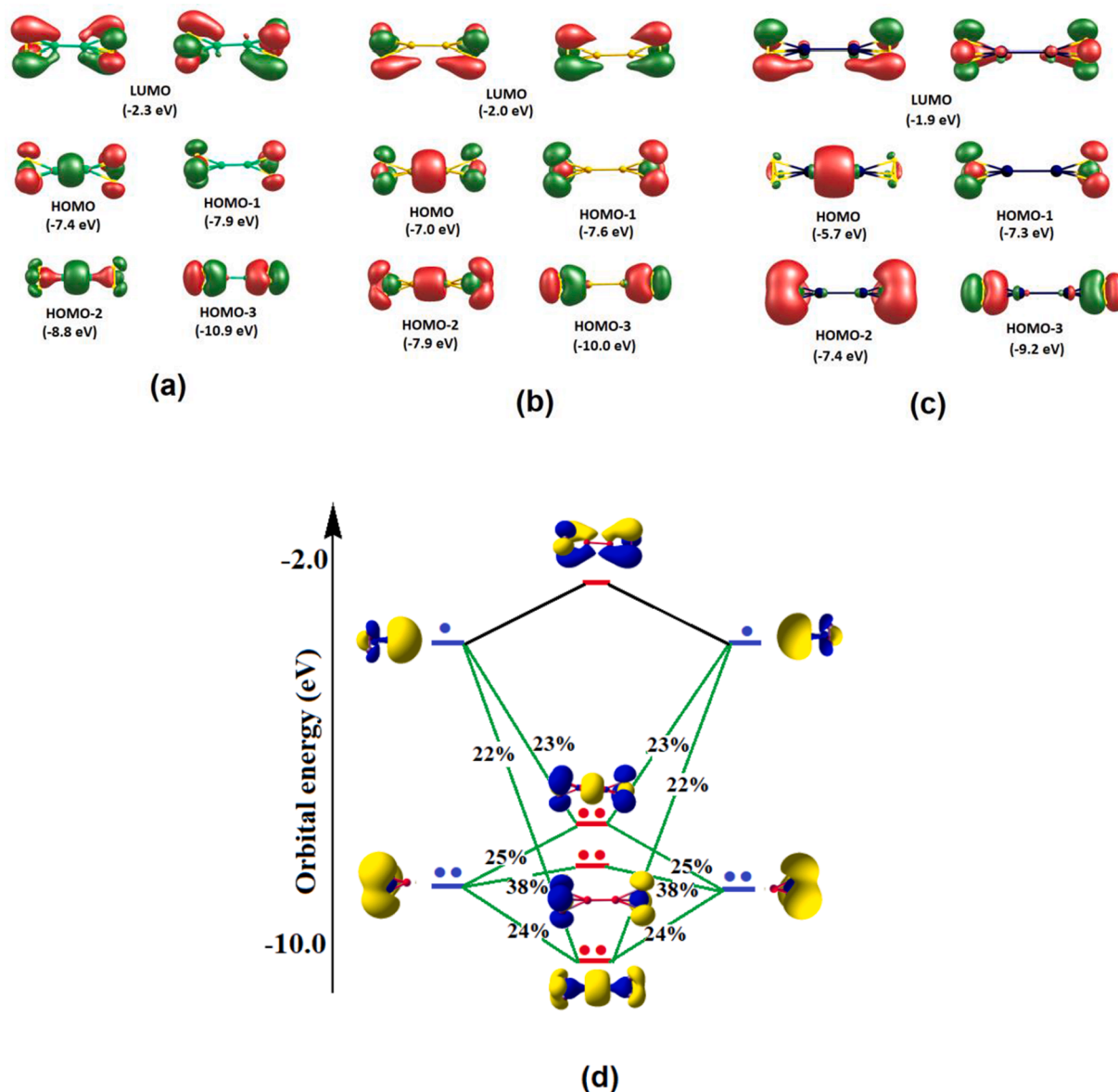


Fig. 2. Kohn-Sham frontier molecular orbitals for (a) B₃-Be-Be-B₃, (b) B₃-Mg-Mg-B₃ and (c) B₃-Ca-Ca-B₃. Contour value used is 0.03. Interaction diagram of B₃-Be-Be-B₃ using charge decomposition analysis is shown in (d). Percentage contributions of each fragment orbitals are also shown.

Table 1

Natural charges, q at Y and B atom in au and electronic configuration of the Y atom.

Molecule	q_Y (au)	q_B (au)	Y electronic configuration
B ₃ -Be-Be-B ₃	0.78	-0.26	[He]2s ^{1.07} 2p ^{0.14}
B ₃ -Mg-Mg-B ₃	0.84	-0.28	[Ne]3s ^{1.10} 3p ^{0.04}
B ₃ -Ca-Ca-B ₃	0.88	-0.29	[Ar]4s ^{1.05} 4p ^{0.03}

(CPs). At this point, the first derivatives of $\rho(\mathbf{r}_c)$ vanishes, i.e., $\nabla\rho(\mathbf{r}_c) = 0$, where

$$\nabla\rho(\mathbf{r}_c) = i\frac{\partial\rho}{\partial x} + j\frac{\partial\rho}{\partial y} + k\frac{\partial\rho}{\partial z}$$

and $\mathbf{r}_c$ is the CP. The Laplacian ($\nabla^2\rho$) plays a major role in the characterization of chemical bonding. For covalent interactions (also referred to as “open-shell” or “sharing” interactions), the electron density at the bond critical point (BCP), ρ_b , is large (>0.2 a.u.) while its laplacian, $\nabla^2\rho$ is large and negative. On the other hand, for closed-shell interactions (e.

Table 2

Electron density, ρ , at the Y-Y bond critical point (bcp), laplacian of electron density, $\nabla^2\rho$, local electronic energy density, $H(r)$, electron localization function, ELF values and $[V(Y,Y)]$ basin populations. All values are in a. u.

Molecule	ρ	$\nabla^2\rho$	$H(r)$	ELF	$[V(Y,Y)]$
B ₃ -Be-Be-B ₃	0.07	-0.11	-0.03	0.98	2.0
B ₃ -Mg-Mg-B ₃	0.03	-0.03	-0.01	0.93	2.0
B ₃ -Ca-Ca-B ₃	0.01	-0.07	-0.02	0.89	1.9
Cp-Be-Be-Cp	0.06	-0.09	-0.02	0.99	2.0
F-Be-Be-F	0.06	-0.10	-0.03	0.99	2.0

g., ionic, van der Waals, or hydrogen bonds), ρ_b is small (<0.10 au) and $\nabla^2\rho$ is positive. But a clear distinction between the closed-shell and covalent type of interaction cannot be done unless determining the local electronic energy density, given by $H(r) = G(r) + V(r)$, where $G(r)$ and $V(r)$ are the local kinetic and potential energy densities. According to Cremer and Kraka [43], positive laplacian, $\nabla^2\rho(r) > 0$, and negative local electronic energy density, $H(r) < 0$ are associated with polar covalent bonds. Table 2 contains the numerical data at Y-Y bond critical

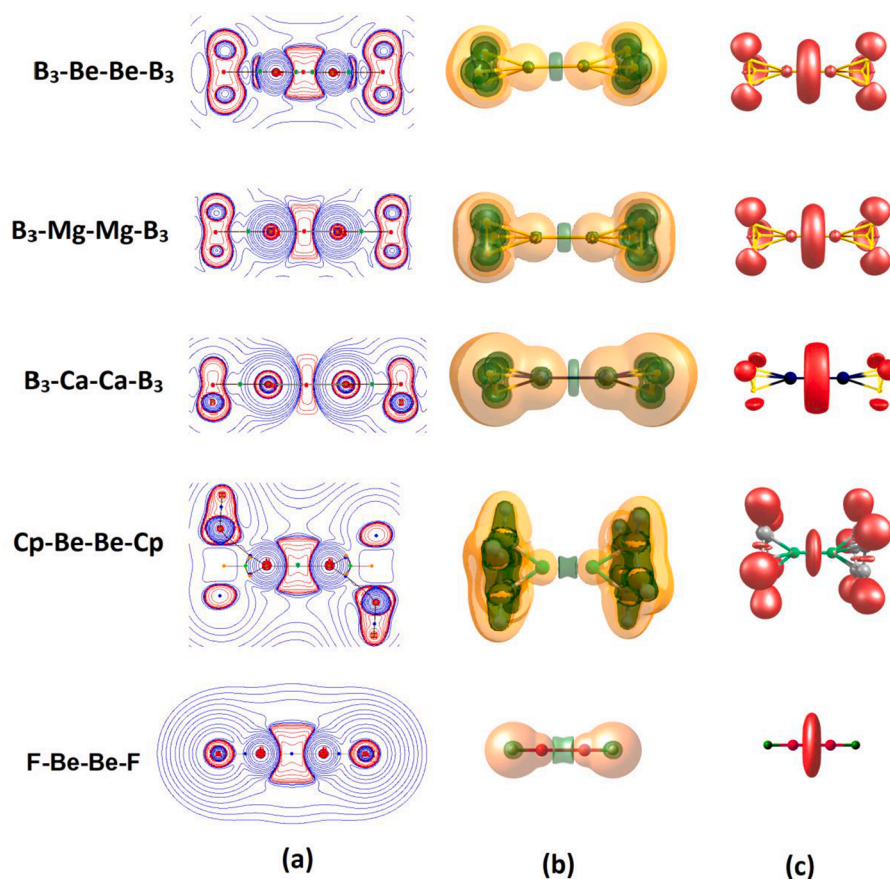
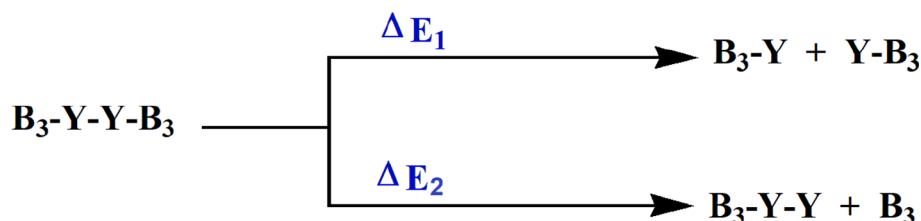


Fig. 3. (a) 2D plot of Laplacian of electron density (red = charge concentration; blue = charge depletion), (b) 3D plot of Laplacian of electron density with contour value = 0.03 and (c) 3D plot of electron localization function. For comparison, F-Be-Be-F and Cp-Be-Be-Cp are also considered. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Scheme 1. Dissociation of the $B_3-Y-Y-B_3$ complex into B_3-Y monomers and B_3-Y-Y and B_3 fragments ($Y = Be, Mg, Ca$) calculated at CCSD(T)/def2-TZVP//M06-2X/def2-TZVP level.

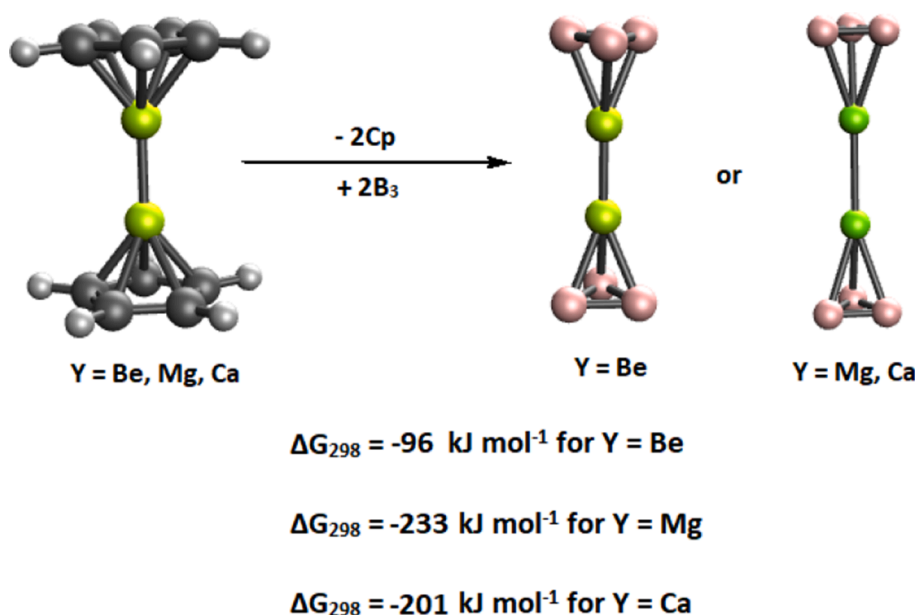
point. The Y-Y bonds are characterized by negative values of laplacian, $\nabla^2\rho$ and negative values of local electronic energy density, $H(r)$. This suggests polar covalent nature of these bonds [37].

Fig. 3 shows the plots of Laplacian of electron density and electron localization function. The molecular graph for all these complexes feature the presence of non-nuclear attractors (NNA, red dots) corresponding to local maxima of electron density, $\rho(r)$, not coinciding with the nuclei position (Fig. 3a). Similar situation has also been observed for Be_2F_2 molecule [12]. In contrast, Cp-Be-Be-Cp does not have a NNA. 3D plot of electron localization function features a disynaptic $[V(Y,Y)]$ basin with population close to $2e^-$. The ELF values at the Y-Y bcps are also close to 1.0.

The dissociation pathways of $B_3-Y-Y-B_3$ complex into B_3-Y monomers and B_3-Y-Y and B_3 as shown in Scheme 1 are also computed. The dissociation into monomers (ΔE_1 , Scheme 1) reflects the strength of Y-Y interaction while the dissociation into B_3-Y-Y and B_3 (ΔE_2) reflects the strength of Y- B_3 interaction. It is evident from Table 3 that Y-Y and B_3-Y

bond strengths decrease in the order $Be > Mg > Ca$. For comparison, we have also considered F-Be-Be-F molecule as it was predicted to have the highest Be-Be bond dissociation energy (BDE) [9,12]. The calculated Be-Be distance in F-Be-Be-F is 2.046 Å at M06-2X/def2-TZVP level of theory which is in excellent agreement with the value (2.048 Å) calculated at CCSD(T)/cc-PVTZ by Frenking and co-workers [9]. Moreover, the calculated value of Be-Be BDE for F-Be-Be-F molecule is in excellent agreement with Brea and coworkers [12]. This also justifies the adequacy of the present level of calculation. It should be noted that the Be-Be BDE value for $B_3-Be-Be-B_3$ complex is 73 kJ mol⁻¹ lower than that of F-Be-Be-F.

Further to investigate the thermodynamics of formation of these complexes, we have used the following reaction. The calculated (M06-2X/def2-TZVP) values of ΔG at 298 K for all these reactions are negative suggesting thermodynamic feasibility of their formation.

**Table 3**

Bond dissociation energies (kJ mol^{-1}) of different pathways as shown in Scheme 1. ^a Calculated at CCSD(T)/cc-pVTZ by Brea and co-workers [12].

Molecule	ΔE_1	ΔE_2
$\text{B}_3\text{-Be-Be-B}_3$	239	301
$\text{B}_3\text{-Mg-Mg-B}_3$	224	207
$\text{B}_3\text{-Ca-Ca-B}_3$	189	173
F-Be-Be-F	312 (313) ^a	723 (736) ^a

4. Conclusion

Quantum chemical calculations has been performed to investigate the possibility of formation of Y-Y ($Y = \text{Be, Mg, Ca}$) interaction in sandwich type complexes $\text{B}_3\text{-Y-Y-B}_3$. The Be complex features a staggered conformation while Mg and Ca prefer eclipsed type conformation. Calculations at CCSD(T) level of theory indicates single reference character of the studied systems as evidenced by the T_1 diagnostic value of 0.02 in all cases. In all these complexes, group 2 metals (Be, Mg and Ca) are monocationic resulting in overall dicationic species, Y_2^{2+} . The B_3 fragment in all cases features a closed shell arrangement which helps in retaining single reference character of the whole system. QTAIM and ELF analyses reveal covalent character of the Y-Y interaction. Thermodynamic consideration also favours their formation.

5. Funding information

No funding was offered for this work.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.poly.2022.115681>.

References

- [1] J.M. Merritt, V.E. Bondybey, M.C. Heaven, *Science* 324 (2009) 1548–1551.
- [2] K. Wang, Y.J. Wang, D.Z. Li, T. Ou, X.Y. Zhao, H.J. Zhai, *Phys. Chem. Chem. Phys.* 18 (2016) 9594–9601.
- [3] K. Nijesh, S. De, P. Parameswaran, *Dalton Trans.* 45 (2016) 7836–7846.
- [4] X.F. Zhao, H. Li, C.X. Yuan, Y.Q. Li, Y.B. Wu, Z.X. Wang, *J. Comput. Chem.* 37 (2016) 261–269.
- [5] C. Yuan, X.F. Zhao, Y.B. Wu, X. Wang, *Angew. Chem. Int. Ed.* 55 (2016) 15651–15655.
- [6] Q. Zhang, W.L. Li, L. Zhao, M. Chen, M. Zhou, J. Li, G. Frenking, *Chem. Eur. J.* 23 (2017) 2035–2039.
- [7] Z.-Z. Qin, Q. Wang, C. Yuan, Y.-T. Yang, X.-F. Zhao, D. Li, P. Liu, Y.-B. Wu, *Dalton Trans.* 47 (2018) 4707–4713.
- [8] W.L. Li, J. Lu, L. Zhao, R. Ponec, D.L. Cooper, J. Li, G. Frenking, *J. Phys. Chem. A* 122 (2018) 2816–2822.
- [9] Z. Cui, W. Yang, L. Zhao, Y. Ding, G. Frenking, *Angew. Chem.* 128 (2016) 7972–7977.
- [10] X. Liao, M. Zhang, S. Yu, Y. Genga, X. Zhanga, Y. Ding, Z. Su, *Phys. Chem. Chem. Phys.* 20 (2018) 23898–23902.
- [11] S.S. Rohman, C. Kashyap, S.S. Ullah, A.K. Guha, L.J. Mazumder, P.K. Sharma, *ChemPhysChem* 20 (2019) 516–518.
- [12] O. Brea, I. Corral, *J. Phys. Chem. A* 122 (2018) 2258–2265.
- [13] Y. Xie, H.F. Schaefer III, E.D. Jemmis, *Chem. Phys. Lett.* 402 (2005) 414–421.
- [14] D.-H. Xing, C.-Q. Xu, Y.-G. Wang, J. Li, *J. Phys. Chem. C* 123 (2019) 10494–10500.
- [15] W.-L. Li, J.-B. Lu, Z.-L. Wang, H.-S. Hu, J. Li, *Inorg. Chem.* 57 (2018) 5499–5506.
- [16] F. Leoni, R. Shi, H. Tanaka, J. Russo, *J. Chem. Phys.* 151 (2019), 044505.
- [17] E. Knuth, S. Schaper, J.P. Toennies, *J. Chem. Phys.* 120 (2003) 235–245.
- [18] T. Jian, X. Chen, S.-D. Li, A.I. Boldyrev, J. Li, L.-S. Wang, *Chem. Soc. Rev.* 48 (2019) 3550–3591.
- [19] H. Zhang, Z. Cao, W. Wu, Y. Mo, *Angew. Chem. Int. Ed.* 57 (2018) 13076–13081.
- [20] M. Wu, E. Luna, J. Puustinen, M. Guina, A. Trampert, *Nanotechnology* 25 (2014), 205605.
- [21] P. Jena, Q. Sun, *Chem. Rev.* 118 (2018) 5755–5870.
- [22] E.N. Ghassemi, J. Larson, Å. Larson, *J. Chem. Phys.* 140 (2014), 154304.
- [23] Y.-J. Wang, L.-Y. Feng, H.-J. Zhai, *Phys. Chem. Chem. Phys.* 21 (2019) 18338–18345.
- [24] Y. Hamrick, R. Van Zee, W. Weltner Jr, *J. Chem. Phys.* 96 (1992) 1767–1775.
- [25] Y. Hamrick, R. Van Zee, W. Weltner Jr, *J. Chem. Phys.* 95 (1991) 3009–3011.
- [26] P. Cias, M. Araki, A. Denisov, J. Maier, *J. Chem. Phys.* 121 (2004) 6776–6778.
- [27] R. Hernandez, J. Simons, *J. Chem. Phys.* 94 (1991) 2961–2967.
- [28] J. Martin, J. Francois, R. Gijbels, *J. Chem. Phys.* 90 (1989) 6469–6485.
- [29] E. Isaac Moreira, B. Brito, J. Higinio Damasceno Jr, J. Teixeira Rabelo, G.-Q. Hai, L. Cândido, *J. Chem. Phys.* 149 (2018), 214303.
- [30] A.N. Alexandrova, A.I. Boldyrev, H.-J. Zhai, L.-S. Wang, *Coord. Chem. Rev.* 250 (2006) 2811–2866.
- [31] L.-M. Yang, J. Wang, Y.-H. Ding, C.-C. Sun, *J. Phys. Chem. A* 111 (2006) 9122–9129.
- [32] H.-J. Zhai, L.-S. Wang, A.N. Alexandrova, A.I. Boldyrev, V.G. Zakrzewski, *J. Phys. Chem. A* 107 (2003) 9319–9328.
- [33] G. Li, L. Meng, H. Zhang, X. Li, Y. Zeng, *Phys. Chem. Chem. Phys.* 22 (2020) 18071–18077.
- [34] Y. Zhao, D.G. Truhlar, *Theor. Chem. Acc.* 120 (2008) 215.
- [35] A.E. Reed, F. Weinhold, L.A. Curtiss, *Chem. Rev.* 88 (2008) 899–926.

- [36] Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian, Inc., Wallingford CT, (2016).
- [37] R.W.F. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford Univ. Press, Oxford, 1990.
- [38] (a) B. Silvi, A. Savin, *Nature* 371 (1994) 683–686;
(b) A.D. Becke, K.E. Edgecombe, *J. Chem. Phys.* 92 (1990) 5397–5403.
- [39] T. Lu, F. Chen, *J. Comput. Chem.* 33 (2012) 580.
- [40] T.J. Lee, P.R. Taylor, *Int. J. Quantum Chem.* 36 (1989) 199–207.
- [41] (a) B. Meng, P.J. Bruna, J.S. Wright, *Mol. Phys.* 79 (1993) 1305–1325;
(b) J.M. Merritt, A.L. Kaledin, V.E. Bondybey, M.C. Heaven, *Phys. Chem. Chem. Phys.* 10 (2008) 4006–4013;
(c) C.W. Bauschlicher, M. Rosi, *Chem. Phys. Lett.* 159 (1989) 485–488.
- [42] S. Dapprich, G. Frenking, *J. Phys. Chem.* 99 (1995) 9352.
- [43] D. Cremer, E. Kraka, *Angew. Chem. Int. Ed.* 23 (1984) 627–628.